SUPPLEMENTARY INFORMATION

Generation of Powerful Tungsten Reductants by Visible Light Excitation

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Experimental section:

General Considerations

All manipulations were performed using a combination of glovebox, high vacuum, and Schlenk techniques under a nitrogen or argon atmosphere.[1] Solvents were purified and degassed by standard procedures. NMR spectra were acquired at room temperature unless otherwise noted through the use of Varian spectrometers. ^{1}H NMR chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for C_6D_5H, 7.26 for $CHCl_3$).[2] ^{13}C NMR spectra are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the solvent (δ 128.06 for C_6D_6 and δ 77.16 for $CDCl_3$).[2] Coupling constants are given in hertz. Infrared spectra were recorded on Nicolet Avatar 370 DTGS spectrometer and are reported in cm^{-1}. Samples for transient absorption and room temperature luminescence measurements were prepared in dry, degassed THF inside a nitrogen-filled glovebox, and placed into the cell of a high-vacuum 1-cm pathlength fused quartz cuvette (Starna Cells) connected to a 10 mL bulb and isolated from atmosphere and the bulb by a high-vacuum Teflon valve (Kontes). All chemicals were obtained from Aldrich. Cobalticenium tetrafluoroborate was synthesized according to the literature method.[3]

Electrochemistry

Cyclic voltammetry studies were carried out with a Princeton Applied Research Parstat 4000 potentiostat/galvanostat using a standard three-electrode configuration. A basal-plane graphite electrode (electrode area = 0.09 cm^2) was used as the working electrode. The electrode sheath was a glass tube; a tinned copper wire was run through the tube and coiled at one end. Silver paint (Flash-Dry Silver Paint, SPI, West Chester, PA) was used to attach the basal-plane carbon (highly-ordered pyrolytic graphite;

GraphiteStore.com) to the coiled wire platform. Finally, the tip of the electrode was sealed with the organic solvent-resistant, electrically insulating, two-part epoxy Loctite Hysol 9460. A platinum wire in a fritted (Vycor) glass tube served as the counter electrode. Ag^+/Ag was used as a quasi-reference electrode, and the ferricenium/ferrocene couple (Cp_2Fe^+/Cp_2Fe) served as an external reference. Measurements were performed at room temperature in THF solutions with 0.1 M $[Bu^n_4N][PF_6]$ as the supporting electrolyte. Sample concentrations were approximately 1 mM. A scan rate of 100 mV/s was used for all cyclic voltammetry measurements unless otherwise noted.

Spectroelectrochemistry

Spectroelectrochemistry studies were conducted using a Pine WaveNow potentiostat (Pine Research Instrumentation, Durham, NC) and an Ocean Optics 2000+ spectrophotometer using fiber optics to transport the light; the spectrometer was controlled with the Ocean Optics SpectraSuite software package. Measurements were performed at room temperature in THF solutions with 0.1 M $[Bu^n_4N][PF_6]$ as the supporting electrolyte. Sample concentration was kept at approximately 15 μM. Oxidation was conducted at -0.15 V vs. Cp_2Fe^+/Cp_2Fe using a platinum flag working electrode, Ag^+/Ag reference electrode, and a fritted (Vycor) platinum wire counter electrode. A quartz cuvette with 1 mm path length was used for absorbance measurements.

Photochemical Methods

UV-visible absorption measurements were carried out using a Cary 50 UV-Vis spectrophotometer in 1 cm pathlength quartz cuvettes. Steady-state and time-resolved spectroscopic measurements were carried out in the Beckman Institute Laser Resource Center (California Institute of Technology). Emission spectra were recorded on a Jobin

Yvon Spec Fluorolog-3-11. Sample excitation was achieved via a xenon arc lamp with wavelength selection provided by a monochromator. Right angle emission was sorted using a monochromator and detected with a Hamamatsu R928P photomultiplier tube with photon counting.

For time-resolved measurements, laser excitation was provided by pulses of 8 ns duration from a Q-switched Nd:YAG laser (Spectra-Physics Quanta-Ray PRO-Series) operating at 10 Hz. The third harmonic was used to pump an optical parametric oscillator (OPO, Spectra-Physics Quanta-Ray MOPO-700) tunable in the visible region to provide laser pulses at 488 nm. Probe light for transient absorption kinetics measurements was provided by a 75-W arc lamp (PTI Model A 1010) that could be operated in continuous wave or pulsed modes. After passing through the sample collinearly with the laser beam, scattered excitation light was rejected by suitable long pass and short pass filters, and probe wavelengths were selected for detection by a double monochromator (Instruments SA DH-10) with 1 mm slits. Transmitted light was detected with a photomultiplier tube (PMT, Hamamatsu R928). The PMT current was amplified and recorded with a GageScope transient digitizer. The data were converted to units of ΔOD ($\Delta OD = -\log_{10}(I/I_0)$, where I is the time-resolved probe-light intensity with laser excitation, and I_0 is the intensity without excitation). Samples measured on microsecond timescale's or faster were stirred continuously and measured using a laser repetition rate of 10 Hz, while samples measured on millisecond timescale's were measured using a laser repetition rate of 10 Hz (10 shots per cycle), stirred for 1 s after each cycle, then allowed to sit until the solution settled (2 s) before the next laser pulse. Data were averaged over approximately 100 shots. All instruments and electronics in these systems were controlled by software written in LabVIEW (National Instruments). Data manipulation was performed with MATLAB R2008a (Mathworks, Inc.).

Probe light for transient absorption spectra was provided by white light flash lamp sources with either nanosecond or microsecond durations. Probe light was

transported via a fiber optic and split by a partial reflector. Approximately 70% of the probe light passed through the sample, the remainder directed around the sample as a reference beam. Sample excitation (λ_{ex} = 488 nm) by the laser beam was collinear with the probe light. Sample and reference beams were coupled by fiber optics to a spectrograph detected using two photodiode arrays (Ocean Optics S1024DW Deep Well Spectrometer), with scattered excitation light rejected by a 488 nm narrow notch filter. The timing synchronization of the laser fire, flashlamp fire, and photodiode array readout were controlled by a series of timing circuits triggered by either a Q-switch advance logic pulse for nanosecond, or a laser lamp sync pulse for microsecond, lamp measurements. The photodiode readout was interfaced with a PC via a National Instruments multifunction input/outpur card. Measurements were made with and without excitation, corrected for dark readout, and corrected for fluorescence when necessary. Difference spectra were averaged over approximately 160 shots. All instruments and electronics in these systems were controlled by software written in LabVIEW (National Instruments).

Synthesis of N-Formyl-2,6-diisopropylaniline

N-Formyl-2,6-diisopropylaniline was prepared by a modification of a literature method.[4] A solution of 2,6-diisopropylaniline (10 mL, 53.0 mmol) in toluene (*ca*. 170 mL) was treated with formic acid (30 mL, 795.1 mmol). The resulting mixture was refluxed in a Dean-Stark apparatus for three hours, at which point additional formic acid (11 mL, 291.5 mmol) was added. After 1 hour of further refluxing (4 hours total), the reaction mixture was allowed to cool to room temperature, and was evaporated *in vacuo* to give a white powder, which was then washed with Et_2O (*ca*. 20 mL) and dried *in vacuo* giving N-formyl-2,6-diisopropylaniline (10.05 g, 92%). Mixture of isomers ^{1}H NMR ($CDCl_3$): 1.20 [d, $^3J_{H\text{-}H}$ = 7 Hz, 12H, ($\underline{Me}_2CH)_2C_6H_3NHCHO$], 1.22 [d, $^3J_{H\text{-}H}$ = 7 Hz, 12H, ($\underline{Me}_2CH)_2C_6H_3NHCHO$], 3.10 [sept, $^3J_{H\text{-}H}$ = 7 Hz, 12H, ($Me_2C\underline{H})_2C_6H_3NHCHO$], 3.23

[sept, $^{3}J_{H\text{-}H}$ = 7 Hz, 12H, $(Me_2C\underline{H})_2C_6H_3NHCHO$], 7.19 [d, $^{3}J_{H\text{-}H}$ = 8 Hz, 2H, $(Me_2CH)_2C_6\underline{H}_3NHCHO$], 7.21 [d, $^{3}J_{H\text{-}H}$ = 8 Hz, 2H, $(Me_2CH)_2C_6\underline{H}_3NHCHO$], 7.29 – 7.35 [m, 3H, $(Me_2CH)_2C_6\underline{H}_3N\underline{H}CHO$], 7.93 [d, $^{3}J_{H\text{-}H}$ = 12 Hz, 1H, $(Me_2CH)_2C_6H_3N\underline{H}CHO$], 8.03 [d, $^{3}J_{H\text{-}H}$ = 12 Hz, 1H, $(Me_2CH)_2C_6H_3NHC\underline{H}O$], 8.37 [d, $^{3}J_{H\text{-}H}$ = 2 Hz, 1H, $(Me_2CH)_2C_6H_3NHC\underline{H}O$]. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): 23.69 [s, 4C, $(\underline{Me}_2CH)_2C_6H_3NHCHO$], 23.72 [s, 4C, $(\underline{Me}_2CH)_2C_6H_3NHCHO$], 28.5 [s, 2C, $(Me_2\underline{C}H)_2C_6H_3NHCHO$], 28.8 [s, 2C, $(Me_2\underline{C}H)_2C_6H_3NHCHO$], 123.6 [s, 2C, $(Me_2CH)_2\underline{C}_6H_3NHCHO$], 123.9 [s, 2C, $(Me_2CH)_2\underline{C}_6H_3NHCHO$], 128.8 [s, 1C, $(Me_2CH)_2\underline{C}_6H_3NHCHO$], 129.0 [s, 1C, $(Me_2CH)_2\underline{C}_6H_3NHCHO$], 129.8 [s, 1C, $(Me_2CH)_2\underline{C}_6H_3NHCHO$], 130.3 [s, 1C, $(Me_2CH)_2\underline{C}_6H_3NHCHO$], 146.2 [s, 2C, $(Me_2CH)_2\underline{C}_6H_3NHCHO$], 146.8 [s, 2C, $(Me_2CH)_2\underline{C}_6H_3NHCHO$], 161.0 [s, 1C, $(Me_2CH)_2C_6H_3NH\underline{C}HO$], 165.8 [s, 1C, $(Me_2CH)_2C_6H_3NH\underline{C}HO$].

Synthesis of 2,6-diisopropylphenylisocyanide (IphNC)

2,6-diisopropylphenylisocyanide was prepared by a modification of a literature method.[4] A colorless solution of N-formyl-2,6-diisopropylaniline (2.00 g, 9.74 mmol) in CH_2Cl_2 (*ca*. 100 mL) was treated with diisopropylamine (4.75 mL, 33.90 mmol), which was then cooled to 0 °C using an ice-water bath. The solution was treated in a dropwise manner with phosphorus(V) oxychloride (1.12 mL, 11.96 mmol) over a period of 20 minutes. The mixture was allowed to warm to room temperature, and stirred at room temperature for 2 hours. At this point, an aqueous solution of Na_2CO_3 (1.5 M, 100 mL, 150 mmol) was added, and the resulting biphasic mixture was allowed to stir for 20 hours. The mixture was diluted with H_2O (*ca*. 50 mL), and the organic and aqueous layers were separated, and the latter was extracted with CH_2Cl_2 (100 mL). The combined organic extracts were dried with Na_2SO_4, and filtered over 50 mL of silica gel. The silica gel was extracted with CH_2Cl_2 (*ca*. 100 mL), and the combined filtrates were evaporated *in vacuo* giving 2,6-diisopropylphenylisocyanide as a pale yellow oil (1.75 g,

96%). ^{1}H NMR (C_6D_6): 1.06 [d, $^{3}J_{H\text{-}H}$ = 7 Hz, 12H, ($\underline{Me}_2CH)_2C_6H_3NC$], 3.38 [sept, $^{3}J_{H\text{-}H}$ = 7 Hz, 2H, ($Me_2C\underline{H})_2C_6H_3NC$], 6.83 [d, $^{3}J_{H\text{-}H}$ = 8 Hz, 2H, $(Me_2CH)_2C_6\underline{H}_3NC$], 6.96 [m, 1H, $(Me_2CH)_2C_6\underline{H}_3NC$]. ^{1}H NMR ($CDCl_3$): 1.28 [d, $^{3}J_{H\text{-}H}$ = 7 Hz, 12H, ($\underline{Me}_2CH)_2C_6H_3NC$], 3.41 [sept, $^{3}J_{H\text{-}H}$ = 7 Hz, 2H, ($Me_2C\underline{H})_2C_6H_3NC$], 7.18 [d, $^{3}J_{H\text{-}H}$ = 8 Hz, 2H, $(Me_2CH)_2C_6\underline{H}_3NC$], 7.32 [t, $^{3}J_{H\text{-}H}$ = 8 Hz, 1H, $(Me_2CH)_2C_6\underline{H}_3NC$]. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): 22.2 [s, 4C, ($\underline{Me}_2CH)_2C_6H_3NC$], 29.5 [s, 2C, ($Me_2\underline{C}H)_2C_6H_3NC$], 122.9 [s, 2C, $(Me_2CH)_2\underline{C}_6H_3NC$], 124.0[m, 1C, $(Me_2CH)_2\underline{C}_6H_3NC$], 129.0 [s, 1C, $(Me_2CH)_2\underline{C}_6H_3NC$], 144.4 [s, 2C, $(Me_2CH)_2\underline{C}_6H_3NC$], 169.3 [s, 2C, $(Me_2CH)_2C_6H_3N\underline{C}$].

Synthesis of W(CNXy)$_6$

$W(CNXy)_6$ was prepared by a modification of a literature method.[5] Sodium mercury amalgam, Na(Hg), was generated by adding small pieces of sodium (58 mg, 2.52 mmol) to mercury (4 g, 19.9 mmol). To the amalgam, a solution of 2,6-dimethylphenylisocyanide (XyNC) (99 mg, 0.76 mmol) in THF (*ca.* 3 mL) was added, followed by a suspension of WCl_6 (50 mg, 0.13 mmol) in THF (*ca.* 3 mL). The resulting dark mixture was stirred vigorously at room temperature for 24 hours, at which point the reaction was filtered, and the filtrate was evaporated *in vacuo* to give a dark-red residue. This residue was extracted into benzene (*ca*. 10 mL), concentrated to approximately half its volume, and left to slowly evaporate giving large, red crystals which were then washed with a small volume of benzene, and dried *in vacuo* giving $W(CNXy)_6$ (60 mg, 43%). ^{1}H NMR (C_6D_6): 2.48 [s, 36H, $(\underline{Me}_2C_6H_3NC)_6W$], 6.76 – 6.81 [m, 18H, $(Me_2C_6\underline{H}_3NC)_6W$]. ^{13}C NMR ($C_6D_6$): $^{13}C\{^{1}H\}$ NMR (C_6D_6): 19.6 [s, 12C, $(\underline{Me}_2C_6H_3NC)_6W$], 125.0 [s, 12C, $(Me_2\underline{C}_6H_3NC)_6W$], 127.8 [s, 6C, $(Me_2\underline{C}_6H_3NC)_6W$], 131.7 [s, 6C, $(Me_2\underline{C}_6H_3NC)_6W$], 133.9 [s, 12C, $(Me_2\underline{C}_6H_3NC)_6W$], 179.9 [s, 6C, $(Me_2C_6H_3N\underline{C})_6W$]. IR Data (KBr disk, cm^{-1}): ν_{CN} = 1934 (s).

Synthesis of $W(CNIph)_6$

Sodium mercury amalgam, Na(Hg) was generated by adding small pieces of sodium (440 mg, 19.1 mmol) to mercury (30 g, 149.6 mmol). To the amalgam, a solution of 2,6-diisopropylphenylisocyanide (1.077 g, 5.75 mmol) in THF (*ca.* 15 mL) was added, followed by a suspension of WCl_6 (379 mg, 0.96 mmol) in THF (*ca.* 15 mL). The resulting dark mixture was diluted with additional THF (*ca.* 40 mL), and was allowed to stir at room temperature for 24 hours, at which point the reaction was filtered, and the filtrate was evaporated *in vacuo* to give a dark-red residue. This residue was extracted into pentane (*ca*. 300 mL), and evaporated *in vacuo*, which was then extracted into benzene (ca. 50 mL), and evaporated to half its volume, and left to slowly evaporate giving red crystals which were then washed with benzene (*ca*. 3 mL), and dried *in vacuo* to give $W(CNIph)_6$ (350 mg, 28%). ^1H NMR (C_6D_6): 1.27 [d, $^3J_{H\text{-}H}$ = 7 Hz, 72H, $\{(\underline{Me}_2CH)_2C_6H_3NC\}_6W$], 3.72 [sept, $^3J_{H\text{-}H}$ = 7 Hz, 12H, $\{(Me_2C\underline{H})_2C_6H_3NC\}_6W$], 6.93 – 6.99 [m, 18H, $\{(Me_2CH)_2C_6\underline{H}_3NC\}_6W$]. $^{13}C\{^1H\}$ NMR (C_6D_6): 22.9 [s, 24C, $\{(\underline{Me}_2CH)_2C_6H_3NC\}_6W$], 30.5 [s, 12C, $\{(Me_2\underline{C}H)_2C_6H_3NC\}_6W$], 30.5 [s, 12C, $\{(Me_2\underline{C}H)_2C_6H_3NC\}_6W$], 123.3 [s, 12C, $\{(Me_2CH)_2\underline{C}_6H_3NC\}_6W$], 125.6 [s, 6C, $\{(Me_2CH)_2\underline{C}_6H_3NC\}_6W$], 129.1 [s, 6C, $\{(Me_2CH)_2\underline{C}_6H_3NC\}_6W$], 143.9 [s, 12C, $\{(Me_2CH)_2\underline{C}_6H_3NC\}_6W$], 177.3 [s, 6C, $\{(Me_2CH)_2C_6H_3N\underline{C}\}_6W$]. IR Data (KBr disk, cm^{-1}): ν_{CN} = 1944 (s).

Table S1. Crystal, intensity collection and refinement data.

	$W(CNIph)_6 \cdot 2(C_6H_6)$
lattice	Triclinic
formula	$C_{90}H_{114}N_6W$
formula weight	1463.72
space group	*P-1*
a / Å	13.1880(6)
b / Å	13.2245(6)
c / Å	13.4292(6)
α / °	69.655(3)
β / °	72.573(3)
γ / °	69.561(3)
V / Å^3	2015.04(16)
Z	1
temperature (K)	200(2)
radiation (λ, Å)	0.71073
ρ (calcd.), g cm^{-3}	1.206
μ (Mo Kα), mm^{-1}	1.480
θ max, deg.	30.26
no. of data collected	54470
no. of data used	12187
no. of parameters	451
R_1 [$I > 2\sigma(I)$]	0.0484
wR_2 [$I > 2\sigma(I)$]	0.1186
R_1 [all data]	0.0497
wR_2 [all data]	0.1196
GOF	1.056

Extinction Coefficient Determinations:

The extinction coefficients for $W(CNXy)_6$ and $W(CNIph)_6$ were determined in THF solutions, using pure THF as the background.

Extinction Coefficients for $W(CNXy)_6$

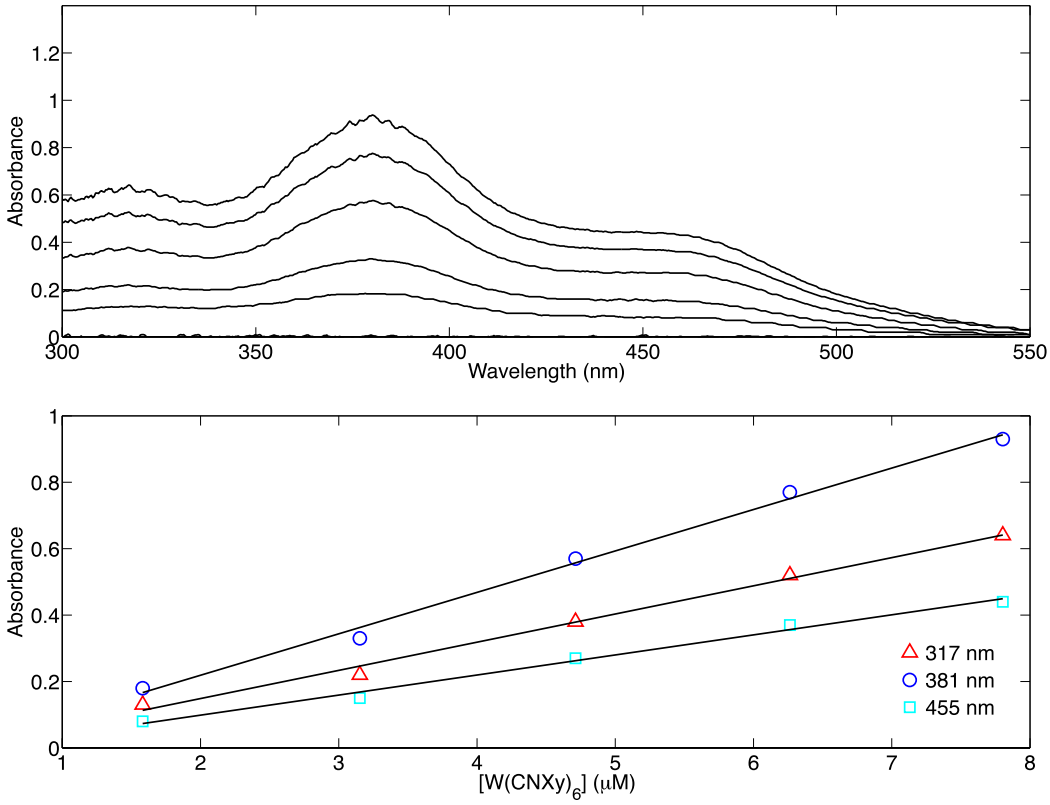


Figure S1. Top: Absorbance spectra of solutions of $W(CNXy)_6$ in THF at different concentrations. Bottom: Plot of the concentration of $W(CNXy)_6$ vs. absorbance at 317, 381 and 455 nm. The extinction coefficients for 317, 381 and 455 nm are 8.49×10^4, 1.25×10^5 and 6.04×10^4 M^{-1} cm^{-1}, respectively.

Extinction Coefficients for $W(CNIph)_6$

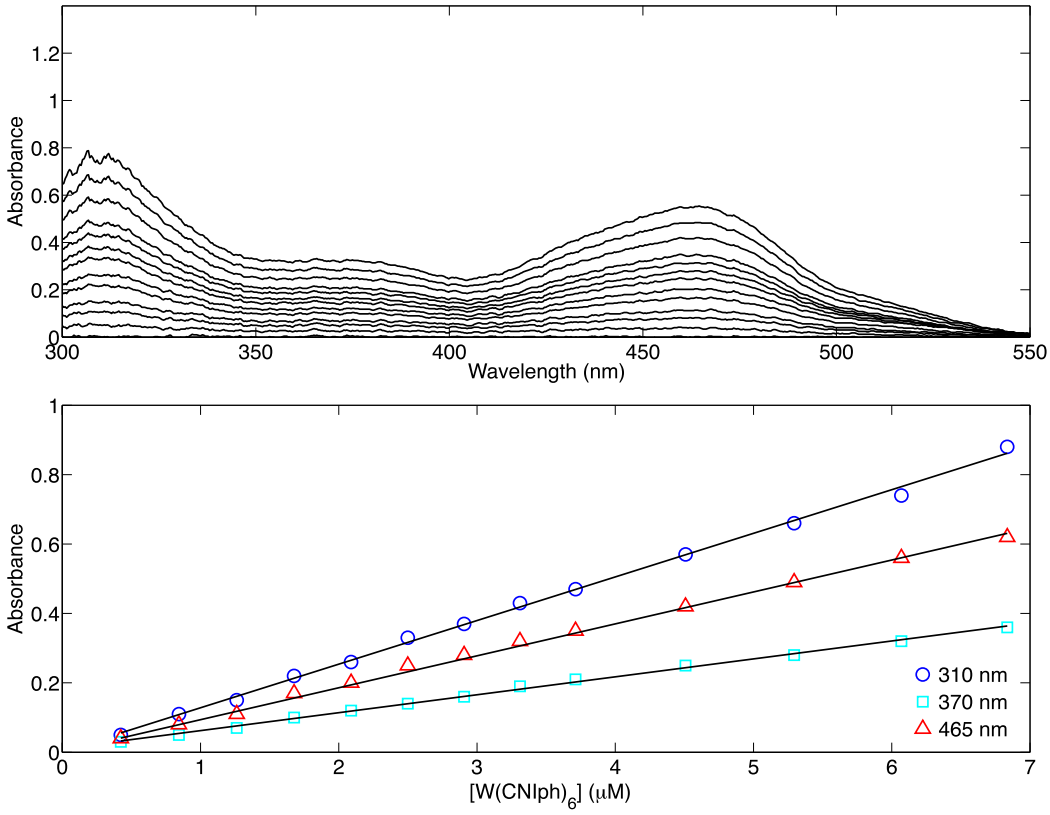


Figure S2. Top: Absorbance spectra of solutions of $W(CNIph)_6$ in THF at different concentrations. Bottom: Plot of the concentration of $W(CNIph)_6$ vs. absorbance at 310, 370 and 465 nm. The extinction coefficients for 310, 370 and 465 nm are 1.26×10^5, 5.17×10^4 and 9.09×10^4 M^{-1} cm^{-1}, respectively.

Low Temperature Emission of $W(CNIph)_6$:

The low temperature emission spectrum of $W(CNIph)_6$ was obtained in a glass formed in 2-MeTHF at 77 K.

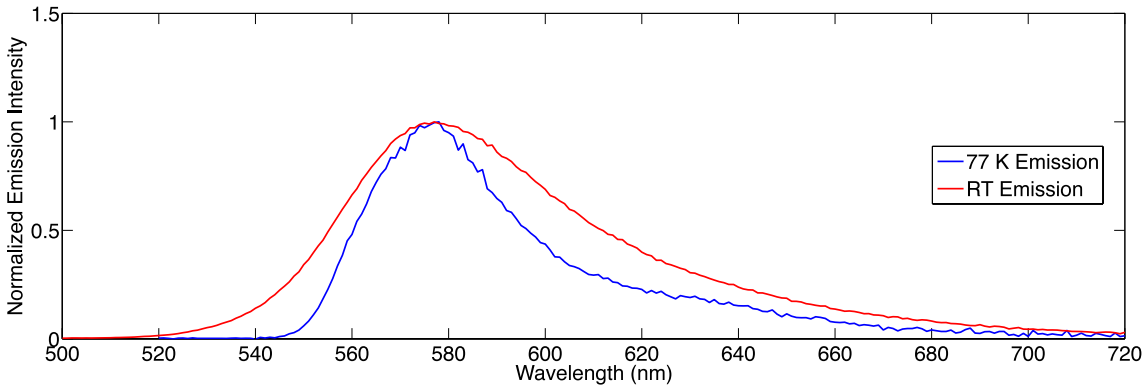


Figure S3. Emission spectra for $W(CNIph)_6$. Room temperature spectrum taken in THF and 77 K spectrum taken in 2-MeTHF.

Excited State Lifetimes:

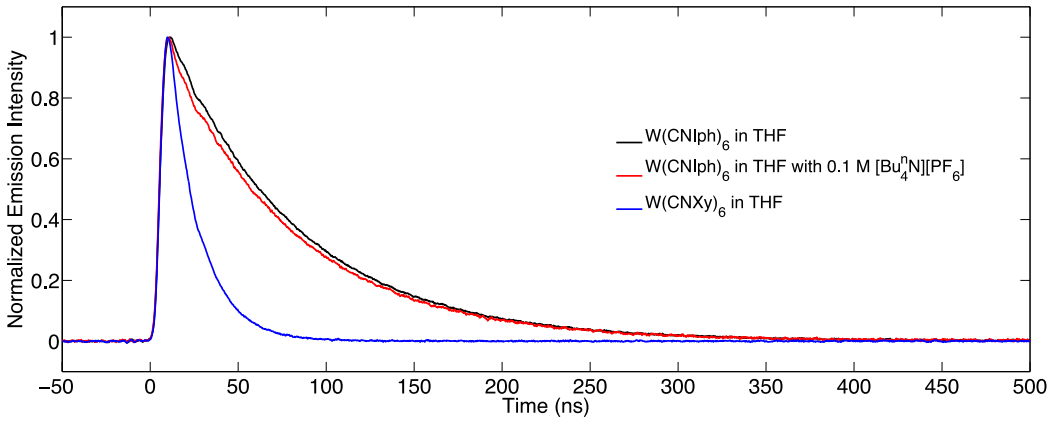


Figure S4. The lifetimes for the excited states of $W(CNIph)_6$ in THF, $W(CNIph)_6$ in 0.1 M THF solution of $[Bu^n_4N][PF_6]$, and $W(CNXy)_6$ are 73, 72 and 17 ns, respectively. λ_{ex} = 488 nm, λ_{em} = 590 nm.

Cyclic Voltammetry Scan Rate Dependence:

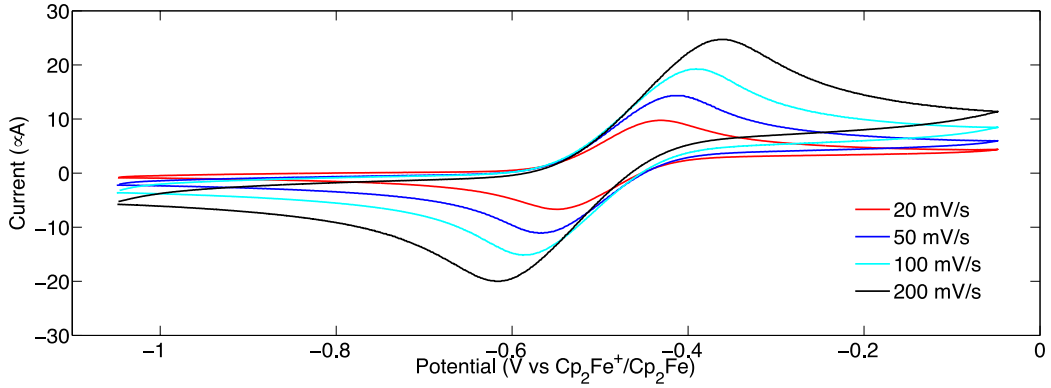


Figure S5. Cyclic voltammograms of $W(CNXy)_6$ in 0.1 M THF solution of $[Bu^n_4N][PF_6]$ at difference scan rates.

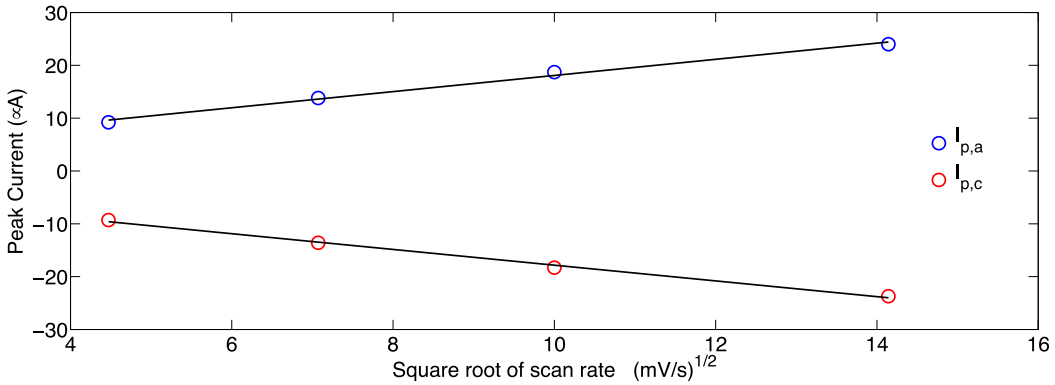


Figure S6. Plot of the square root of scan rate vs. the anodic and cathodic peak currents for $W(CNXy)_6$ in 0.1 M THF solution of $[Bu^n_4N][PF_6]$ at difference scan rates.

Table S2. Scan rate dependence data for $W(CNXy)_6$ in 0.1 M THF solution of $[Bu^n_4N][PF_6]$

Scan Rate (mV/s)	$I_{p,a}$ (μA)	$I_{p,c}$ (μA)	$\lvert I_{p,a}/I_{p,c} \rvert$
20	9.2	-9.3	1.01
50	13.8	-13.6	0.99
100	18.7	-18.3	0.98
200	24.0	-23.7	0.99

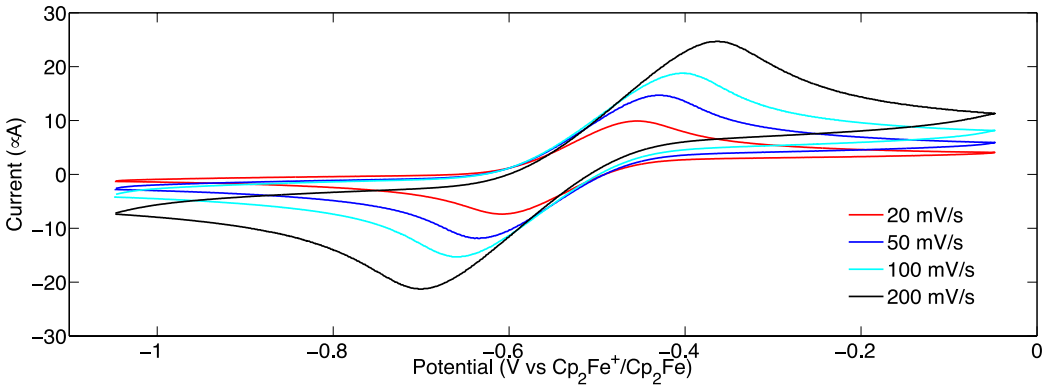


Figure S7. Cyclic voltammograms of $W(CNIph)_6$ in 0.1 M THF solution of $[Bu^n_4N][PF_6]$ at difference scan rates.

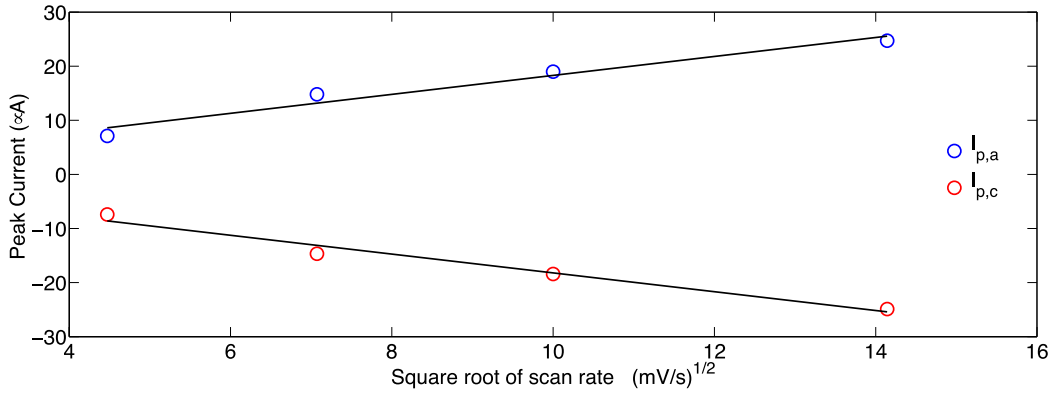


Figure S8. Plot of the square root of scan rate vs. the anodic and cathodic peak currents for $W(CNIph)_6$ in 0.1 M THF solution of $[Bu^n_4N][PF_6]$ at difference scan rates.

Table S3. Scan rate dependence data for $W(CNIph)_6$ in 0.1 M THF solution of $[Bu^n_4N][PF_6]$

Scan Rate (mV/s)	$I_{p,a}$ (μA)	$I_{p,c}$ (μA)	$\lvert I_{p,a}/I_{p,c} \rvert$
20	7.1	-7.3	1.04
50	14.8	-14.7	0.99
100	19.0	-18.4	0.97
200	24.7	-24.9	1.01

Spectroelectrochemical analysis for the oxidation of $W(CNIph)_6$

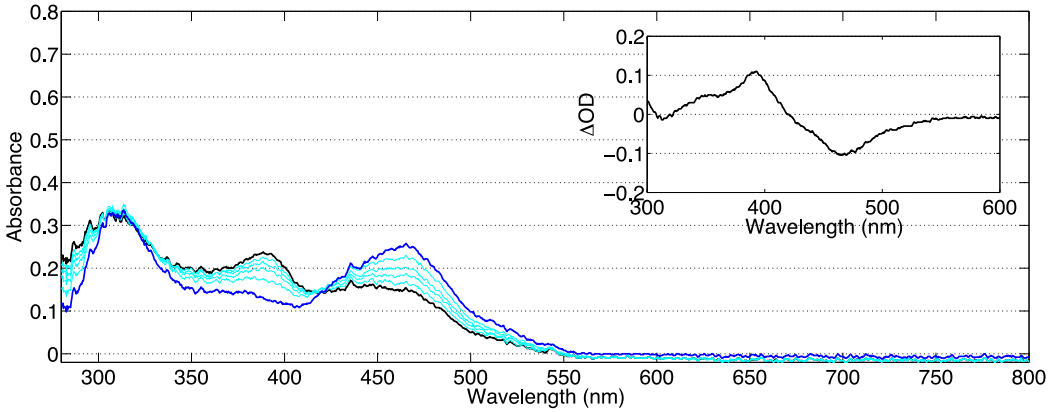


Figure S9. Absorption spectra obtained during electrochemical oxidation of $W(CNIph)_6$ (blue) to give $[W(CNIph)_6]^+$ (black). Oxidation was performed at -0.15 V vs. Cp_2Fe^+/Cp_2Fe at room temperature in THF with 0.1 M $[Bu^n_4N][PF_6]$ as the supporting electrolyte. Experiments were conducted in a 1 mm path length quartz cuvette with a platinum mesh electrode. Inset: Predicted difference absorption spectrum for conversion of $W(CNIph)_6$ to $[W(CNIph)_6]^+$.

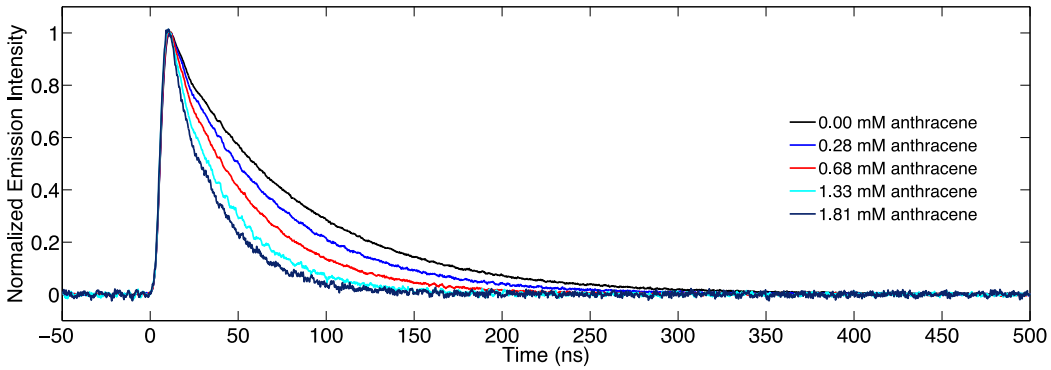
Stern-Volmer Analyses:

Anthracene quenching of *W(CNIph)$_6$ in THF.

Anthracene (43.3 mg, 0.243 mmol) was dissolved in THF (2 mL, 122 mM). 50 μL of the 122 mM solution was diluted with THF to a total volume of 1.05 mL to give an anthracene concentration of 5.78 mM (solution A). This solution was added to THF solutions containing W(CNIph)$_6$ (*ca.* 3 μM) as described in the table below.

Table S4. Solution preparation for Stern-Volmer analysis of anthracene quenching of *W(CNIph)$_6$ in THF.

Volume of solution A added (μL)	Total Volume (mL)	[Anthracene] (mM)	Lifetime (ns)
0	1.50	0.0	73
50	1.05	0.28	60
120	1.02	0.68	46
240	1.04	1.33	36
320	1.02	1.81	30



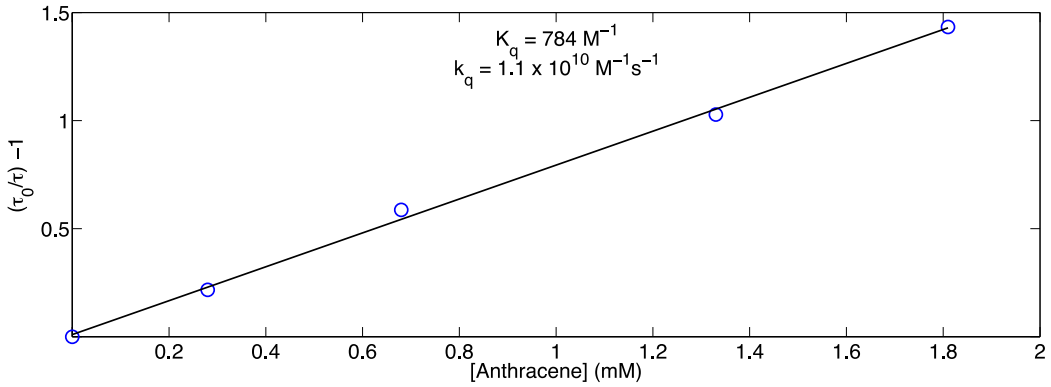


Figure S10. Quenching of *W(CNIph)$_6$ by anthracene in THF. λ_{ex} = 470 nm, λ_{em} = 570 nm. Top: Time-resolved luminescence decays at different anthracene concentrations. Bottom: Stern-Volmer analysis.

Anthracene quenching of *W(CNIph)$_6$ in *ca.* 0.1 M THF solution of [Bu$^n_4$N][PF$_6$]. Anthracene (22.6 mg, 0.127 mmol) was dissolved in THF (4 mL, 31.7 mM, solution B). 20, 40, 70, 120 and 170 μL of this solution was added to a 0.1 M [Bu$^n_4$N][PF$_6$] THF solution (1.5 mL) containing W(CNIph)$_6$ (*ca.* 3 μM). The concentration of [Bu$^n_4$N][PF$_6$] varied from 0.10 to 0.09 M.

Table S5. Solution preparation for Stern-Volmer analysis of anthracene quenching of *W(CNIph)$_6$ in THF with [Bu$^n_4$N][PF$_6$].

Volume of solution B added (μL)	Total Volume (mL)	[Anthracene] (mM)	Lifetime (ns)
0	1.50	0.0	71
20	1.52	0.42	54
40	1.54	0.82	44
70	1.57	1.41	34
120	1.62	2.35	26
170	1.67	3.23	21

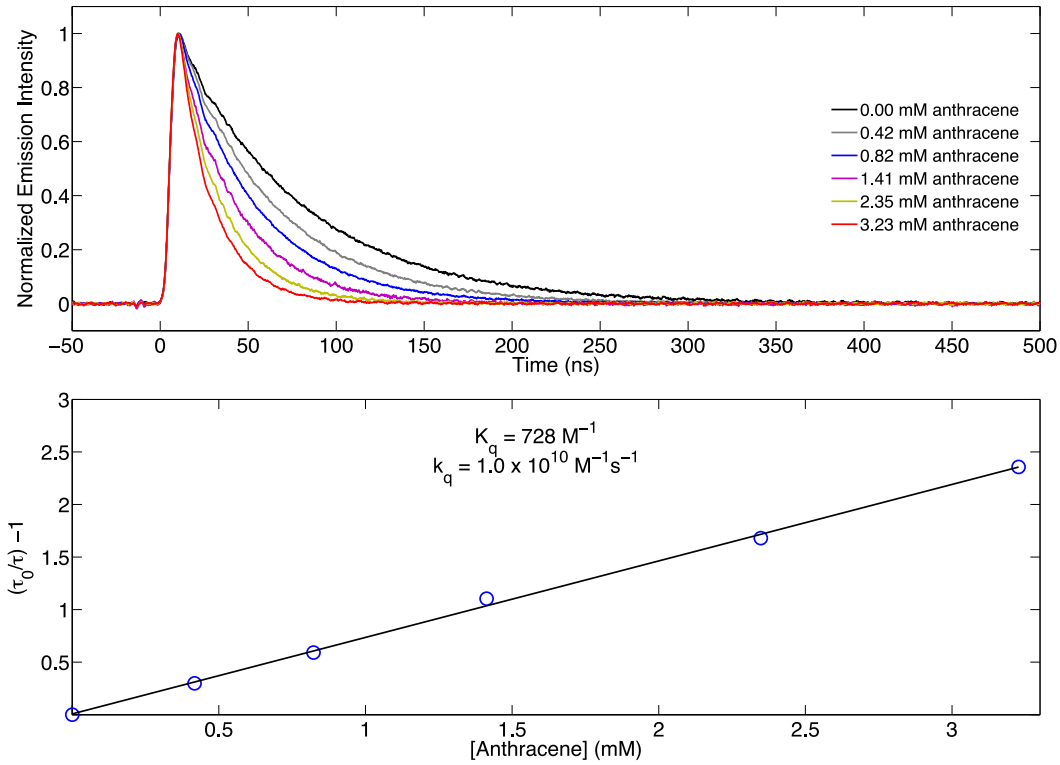


Figure S11. Quenching of *W(CNIph)$_6$ by anthracene in *ca.* 0.1 M THF solution of [Bu$^n_4$N][PF$_6$]. λ_{ex} = 488 nm, λ_{em} = 590 nm. Top: Time-resolved luminescence decays at different anthracene concentrations. Bottom: Stern-Volmer analysis.

Benzophenone quenching of *W(CNIph)$_6$ in *ca.* 0.1 M THF solution of [Bu$^n_4$N][PF$_6$]. Benzophenone (20.8 mg, 0.114 mmol) was dissolved in THF (4 mL, 28.5 mM, solution C). 20, 40, 70, 120 and 170 μL of this solution was added to a 0.1 M [Bu$^n_4$N][PF$_6$] THF solution (1.5 mL) containing W(CNIph)$_6$ (*ca.* 3 μM). The concentration of [Bu$^n_4$N][PF$_6$] varied from 0.10 to 0.09 M.

Table S6. Solution preparation for Stern-Volmer analysis of benzophenone quenching of *W(CNIph)$_6$ in THF with [Bu$^n_4$N][PF$_6$].

Volume of solution C added (μL)	Total Volume (mL)	[Benzophenone] (mM)	Lifetime (ns)
0	1.50	0.0	69
20	1.52	0.38	53
40	1.54	0.74	44
70	1.57	1.27	35
120	1.62	2.11	26
170	1.67	2.91	22

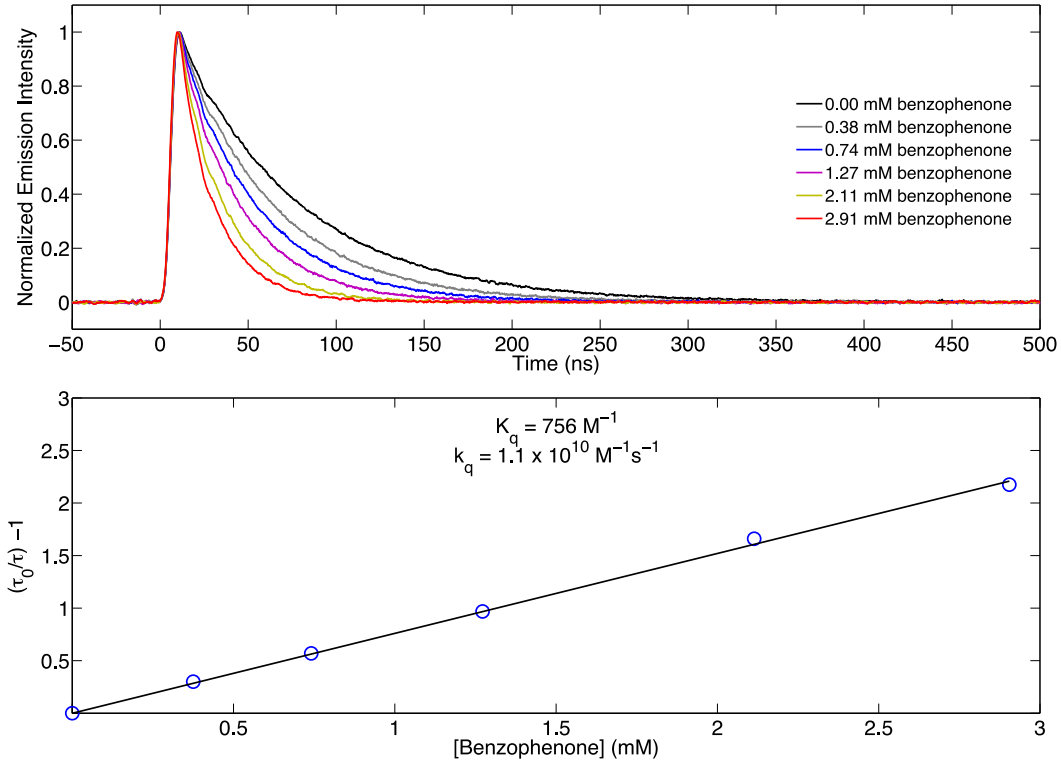


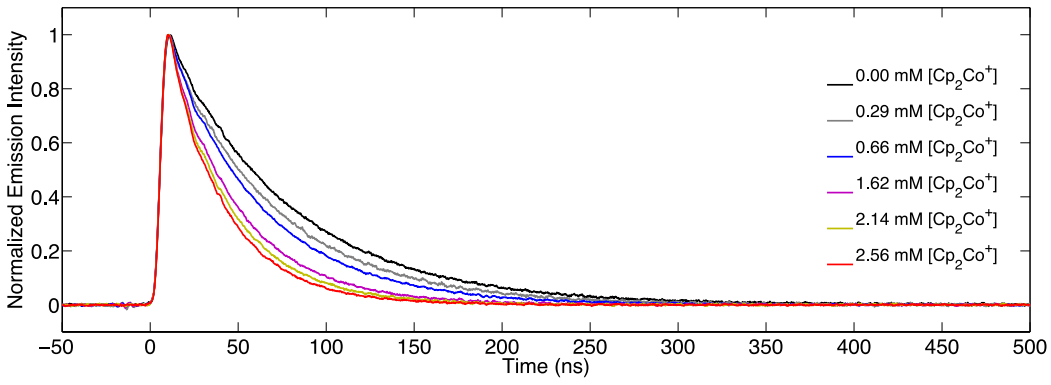
Figure S12. Quenching of *W(CNIph)$_6$ by benzophenone in *ca.* 0.1 M THF solution of [Bu$^n_4$N][PF$_6$]. λ_{ex} = 488 nm, λ_{em} = 590 nm. Top: Time-resolved luminescence decays at different benzophenone concentrations. Bottom: Stern-Volmer analysis.

Cobalticenium quenching of *W(CNIph)$_6$ in *ca.* 0.12 – 0.17 M THF solution of [Bu$^n_4$N][PF$_6$].

Cobalticenium tetrafluoroborate[6] (9.9 mg, 0.04 mmol) was dissolved in THF (4 mL, 8.97 mM, solution D). 50, 120, 330, 470 and 600 μL of this solution was added to a 0.17 M [Bu$^n_4$N][PF$_6$] THF solution (1.5 mL) containing W(CNIph)$_6$ (*ca.* 3 μM). The concentration of [Bu$^n_4$N][PF$_6$] varied from 0.17 to 0.12 M.

Table S7. Solution preparation for Stern-Volmer analysis of cobalticenium quenching of *W(CNIph)$_6$ in THF with [Bu$^n_4$N][PF$_6$].

Volume of solution D added (μL)	Total Volume (mL)	[Cp$_2$Co$^+$] (mM)	Lifetime (ns)
0	1.50	0.0	69
50	1.55	0.29	61
120	1.62	0.66	54
330	1.83	1.62	41
470	1.97	2.14	36
600	2.10	2.56	33



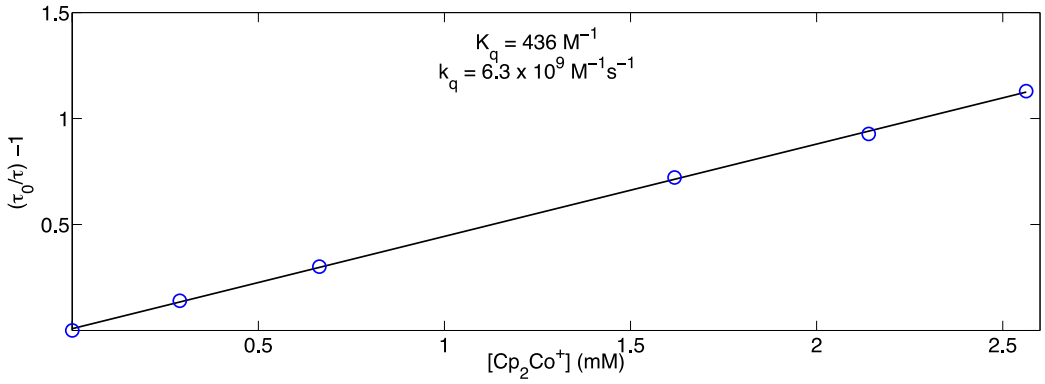


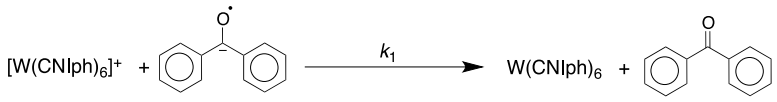
Figure S13. Quenching of *W(CNIph)$_6$ by cobalticenium in *ca.* 0.12 – 0.17 M THF solution of [Bu$^n_4$N][PF$_6$]. λ_{ex} = 488 nm, λ_{em} = 590 nm. Top: Time-resolved luminescence decays at different cobalticenium concentrations. Bottom: Stern-Volmer analysis.

Kinetics Fitting:

Benzophenone (0.1 M $[Bu^n_4N][PF_6]$ in THF):

$[W(CNIph)_6]^+$ and benzophenone$^{-\cdot}$ are generated in the quenching reaction between *W and benzophenone.

Below is the fit data of the back ET reaction between $[W(CNIph)_6]^+$ and benzophenone$^{-\cdot}$ back to ground state.



Approximations:

$\varepsilon_{W^+,460} - \varepsilon_{W^0,460} = 5.0 \times 10^4\ M^{-1}\ cm^{-1}$.

$\varepsilon_{Ph_2CO^{-\cdot},720} = 1.0 \times 10^3\ M^{-1}\ cm^{-1}$ ($\varepsilon_{Ph_2CO,720} = 0.0\ M^{-1}\ cm^{-1}$).

Assume that ΔOD is dominated by tungsten compounds at 460 nm and dominated by benzophenone$^{-\cdot}$ at 720 nm.

Fitting equations:

$$\Delta OD_{460\ nm} = \frac{1}{[W(CNIph)_6^+]_0^{-1} + k_1 t}$$

$$\Delta OD_{720\ nm} = \frac{1}{[Ph_2CO^-]_0^{-1} + k_1 t}$$

$[W]_0 = 4.2\ \mu M$

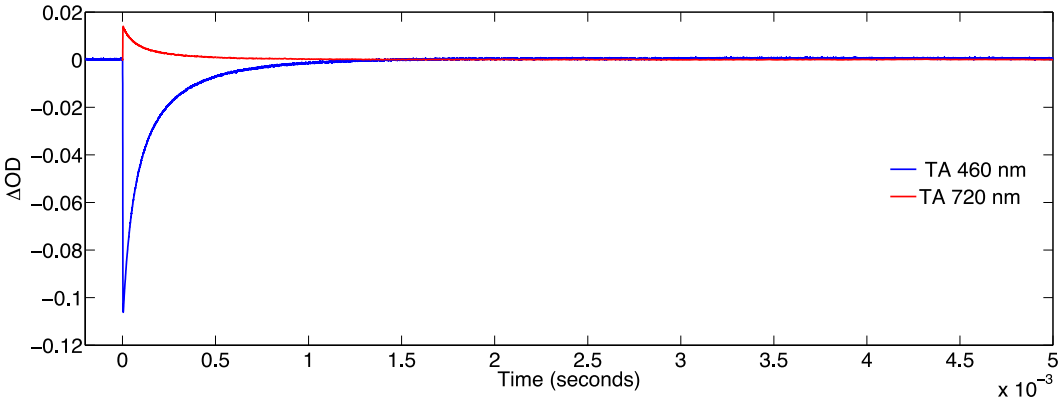


Figure S14. 460 and 720 nm TA signals associated with back ET.

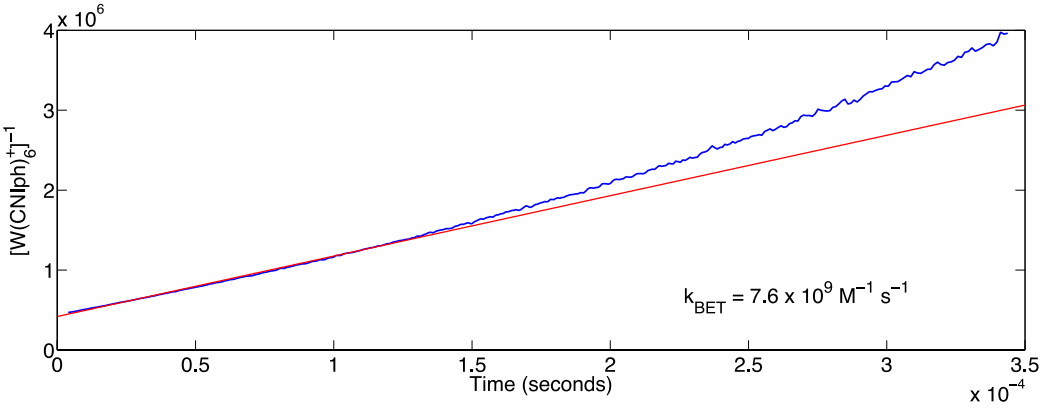


Figure S15. Plot of 1/[W(CNIph)$_6$]$^+$ (460 nm TA).

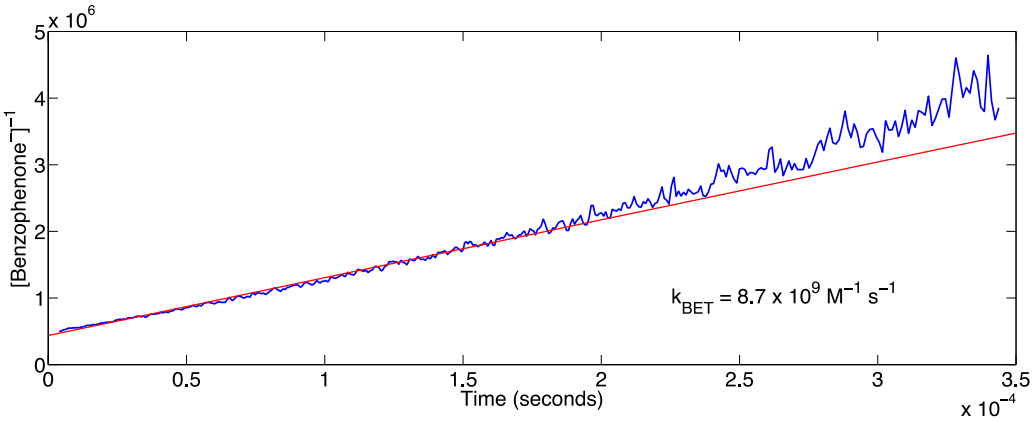


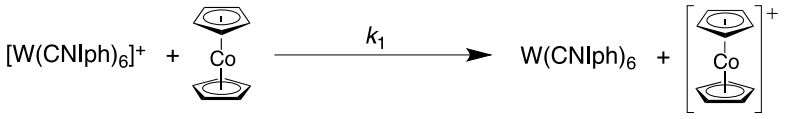
Figure S16. Plot of 1/[benzophenone]$^-$ (720 nm TA).

The back electron transfer kinetics, as analyzed above, give a second-order rate constant of *ca*. 8×10^9 M^{-1} s^{-1}.

Cobalticenium (0.1 M [Bu^n_4N][PF_6] in THF):

$[W(CNIph)_6]^+$ and cobaltocene are generated in the quenching reaction between *W and cobalticenium.

Below is the fit data of the back ET reaction between $[W(CNIph)_6]^+$ and cobaltocene back to ground state.



Approximations:

$\varepsilon_{W^+,460} - \varepsilon_{W^0,460} = 5.0 \times 10^4\ M^{-1}\ cm^{-1}$.

Assume that ΔOD is dominated by tungsten compounds at 460 nm as the extinction coefficeints for cobaltocene and cobalticenium are small (< 500 $M^{-1}\ cm^{-1}$).[7]

Fitting equations:

$$\Delta OD_{460\ nm} = \frac{1}{[W(CNIph)_6^+]_0^{-1} + k_1 t}$$

$[W]_0 = 4.2\ \mu M$

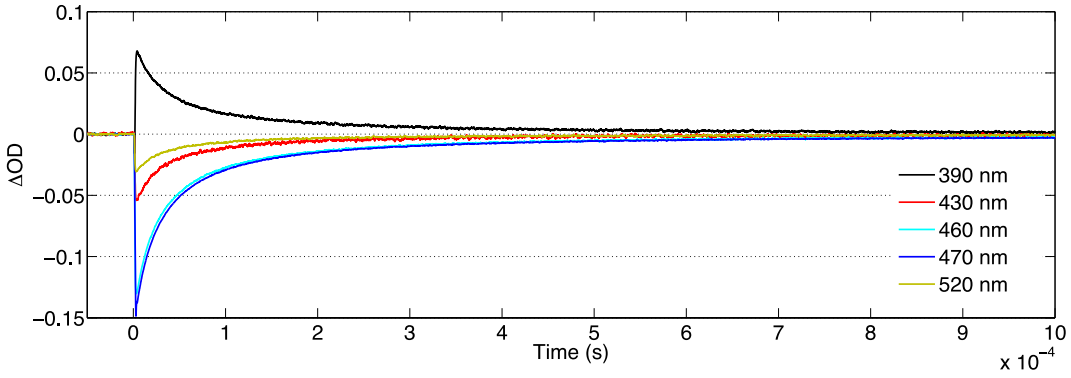


Figure S17. Single wavelength TA signals associated with the back ET.

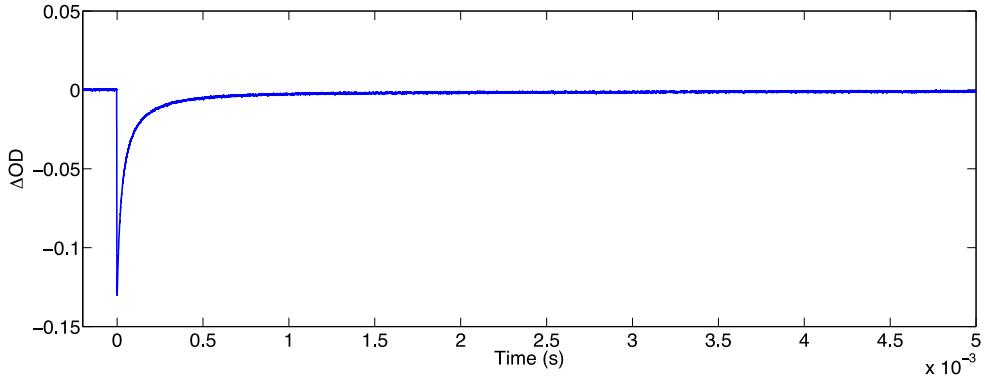


Figure S18. TA signal at 460 nm associated with the back ET.

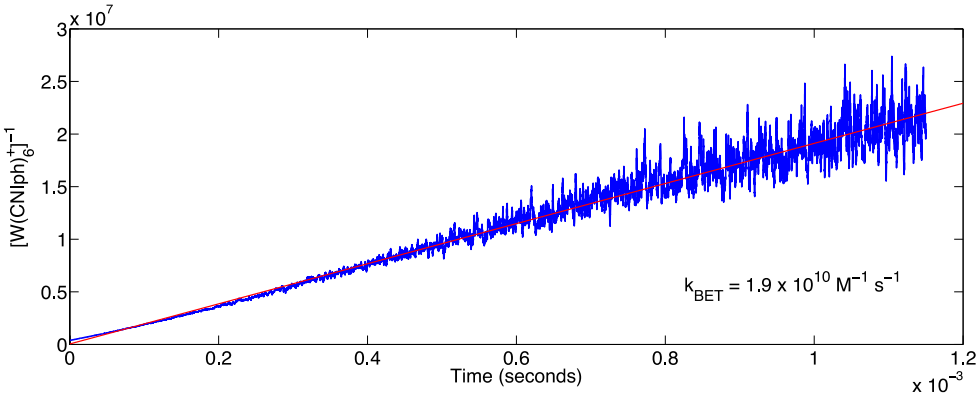


Figure S19. Plot of 1/$[W(CNIph)_6]^+$ (460 nm TA).

The back electron transfer kinetics, as analyzed above, give a second-order rate constant of *ca*. 2×10^{10} M^{-1} s^{-1}.

NMR Spectra:

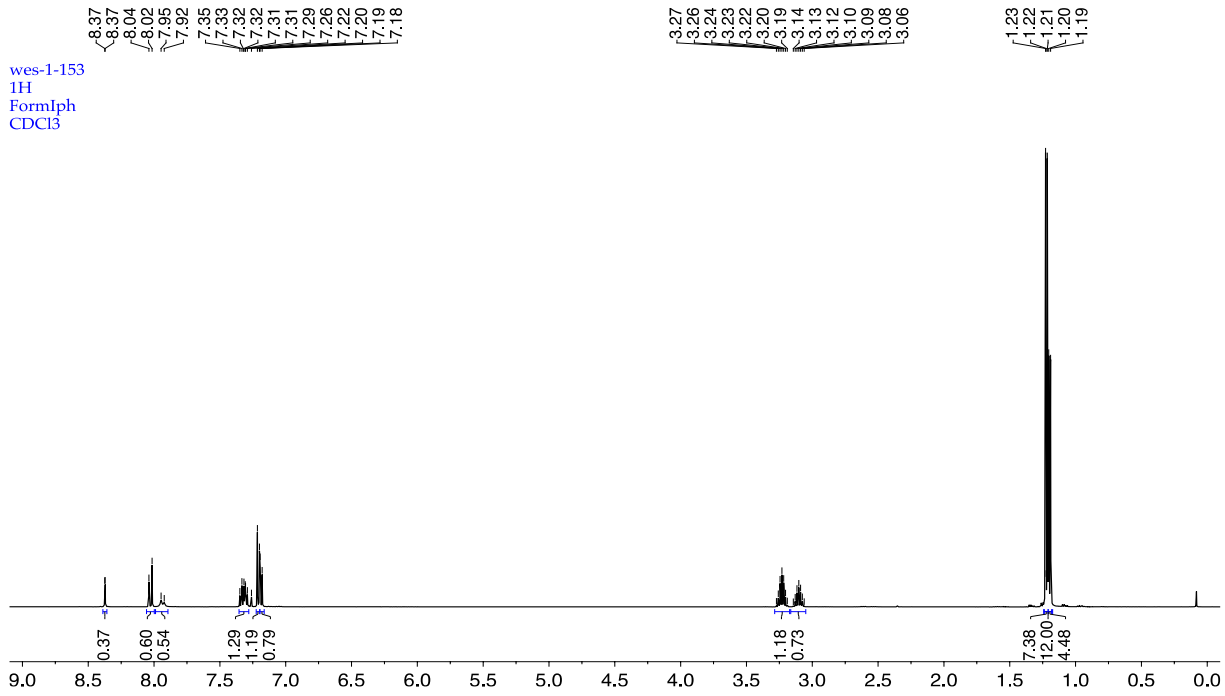


Figure S20. ^{1}H *NMR of N-formyl-2,6-diisopropylaniline*

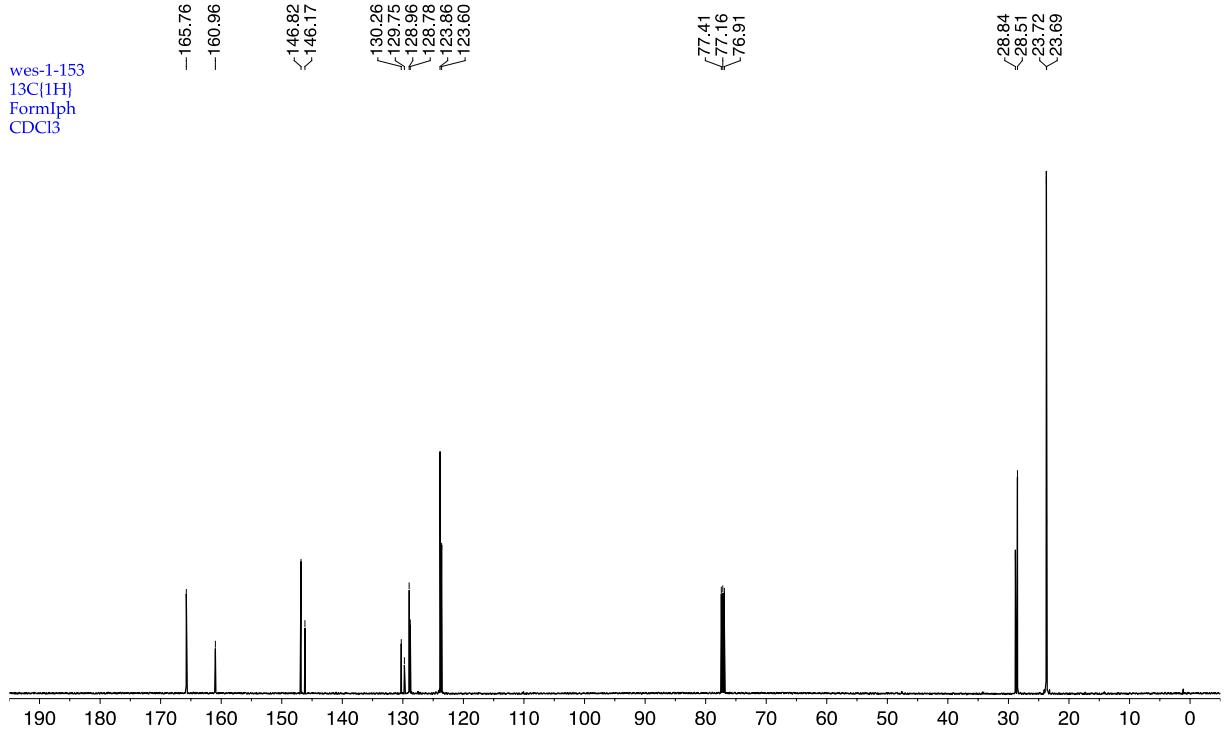


Figure S21. *$^{13}C\{^{1}H\}$ NMR of N-formyl-2,6-diisopropylaniline*

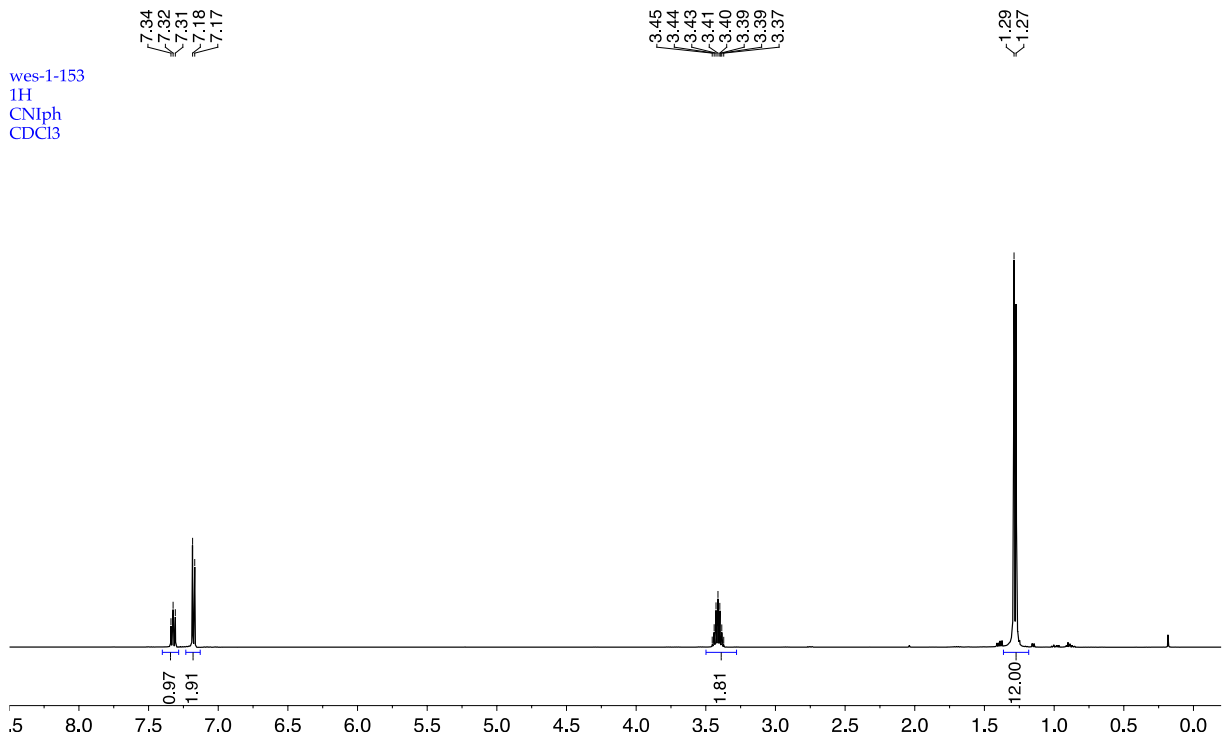


Figure S22. *^{1}H NMR of 2,6-diisopropylphenylisocyanide*

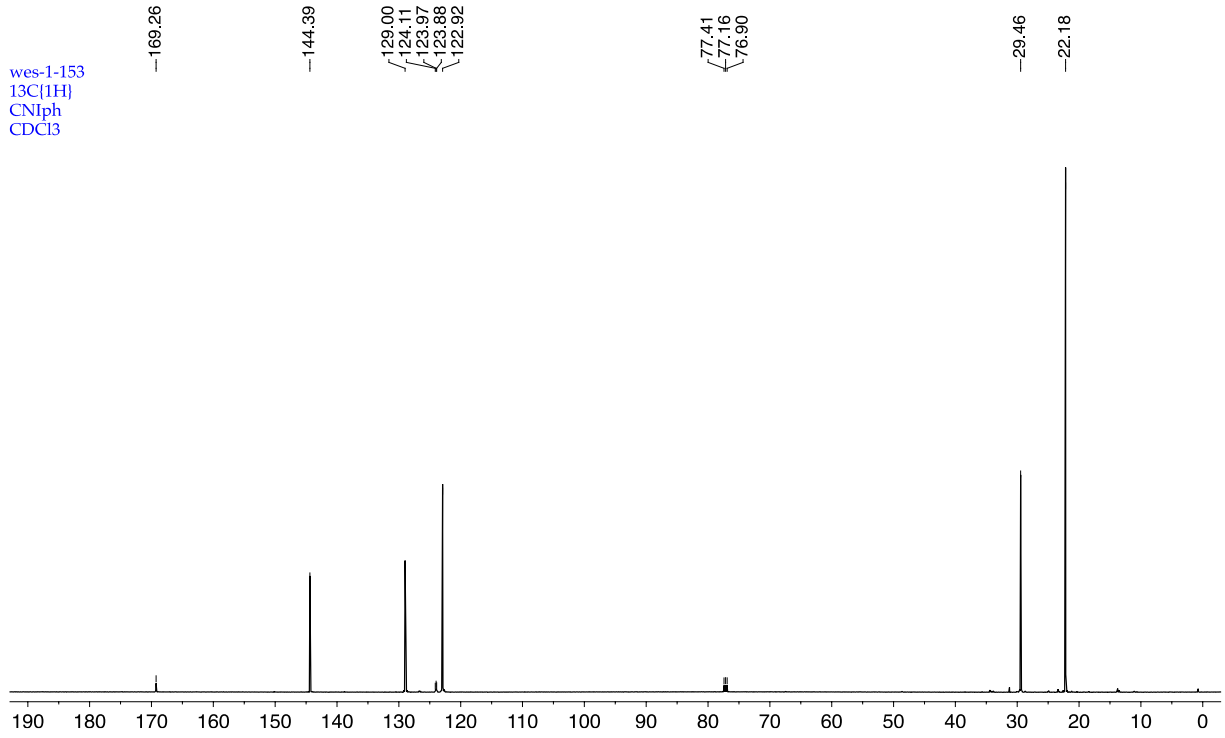


Figure S23. *$^{13}C\{^{1}H\}$ NMR of 2,6-diisopropylphenylisocyanide*

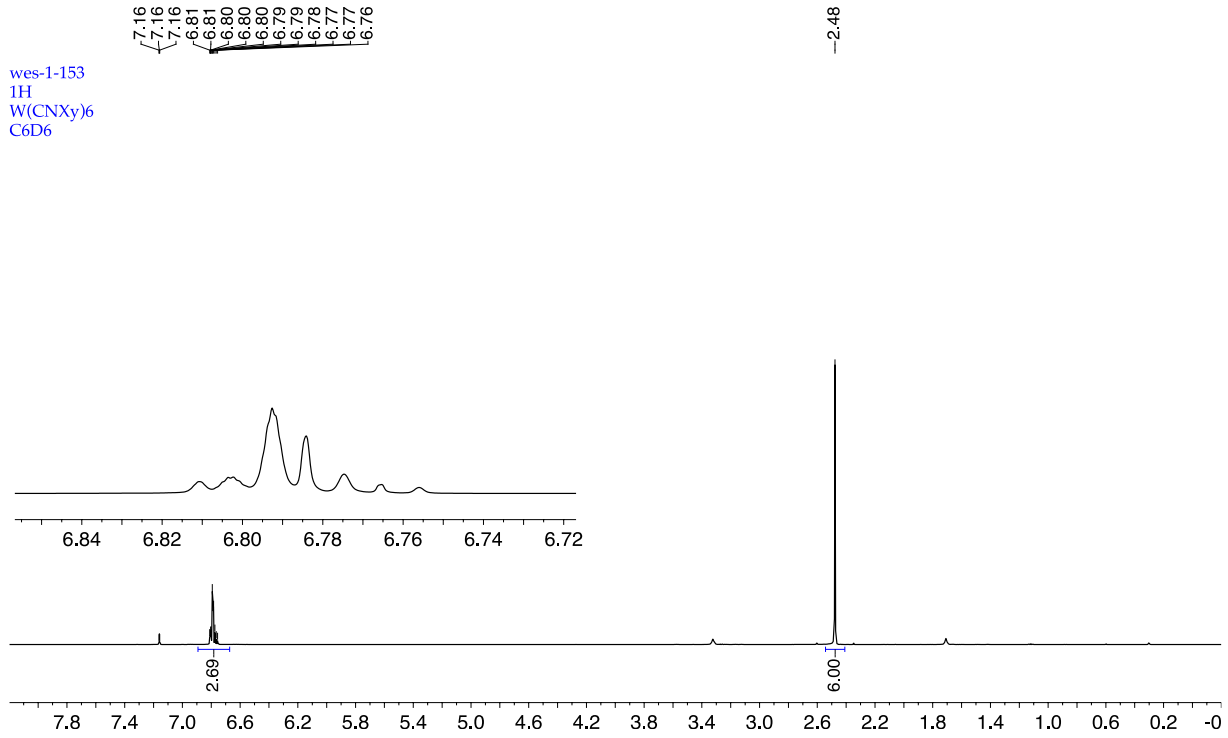


Figure S24. *^{1}H NMR of $W(CNXy)_6$*

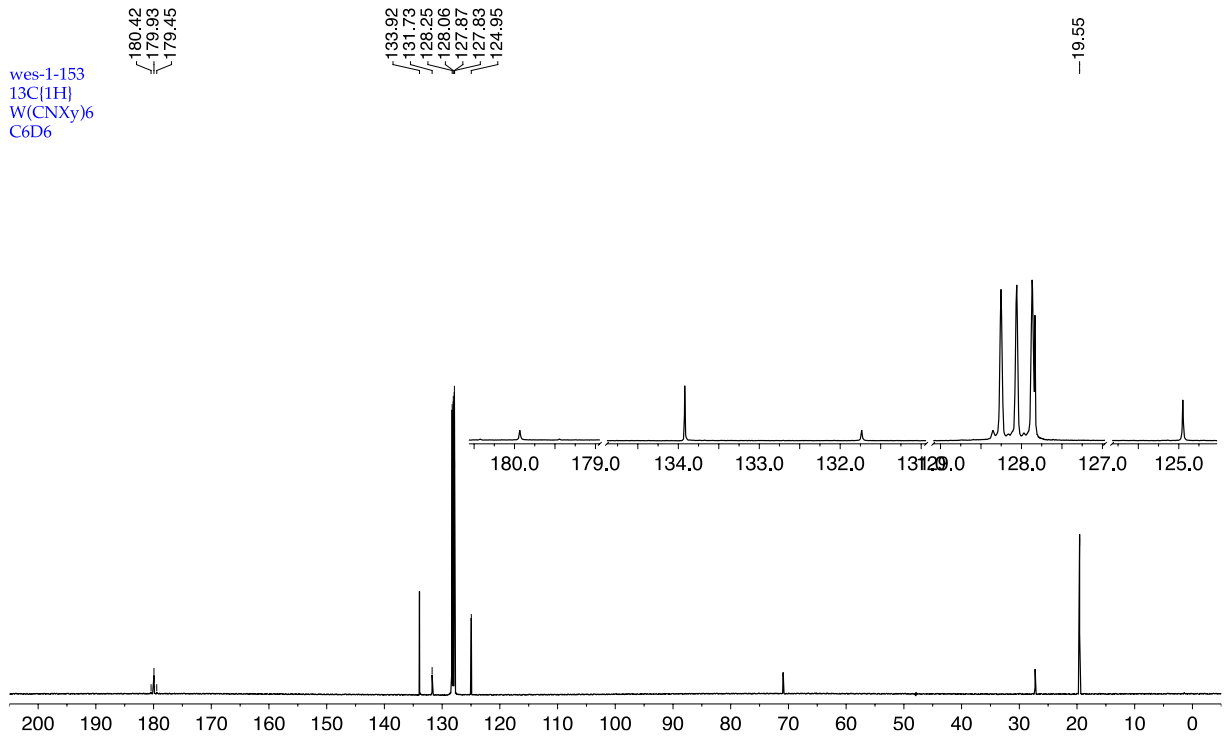


Figure S25. *$^{13}C\{^{1}H\}$ NMR of $W(CNXy)_6$*

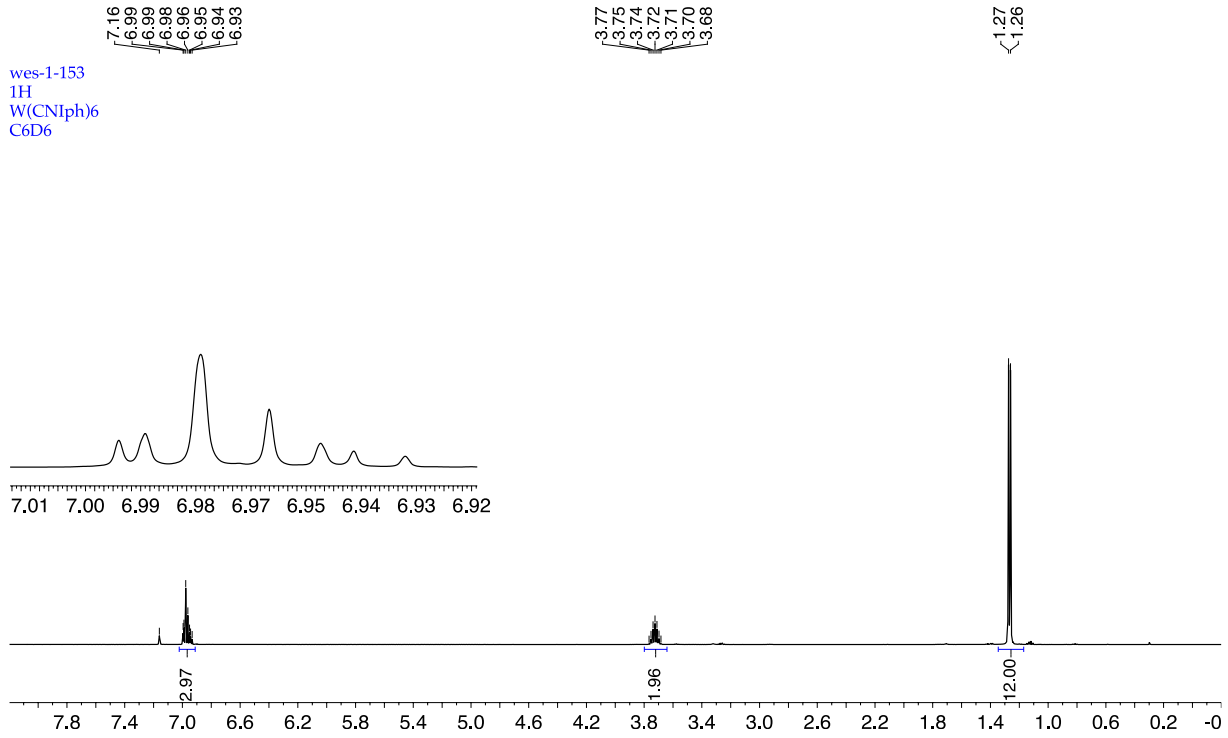


Figure S26. *^{1}H NMR of $W(CNIph)_6$*

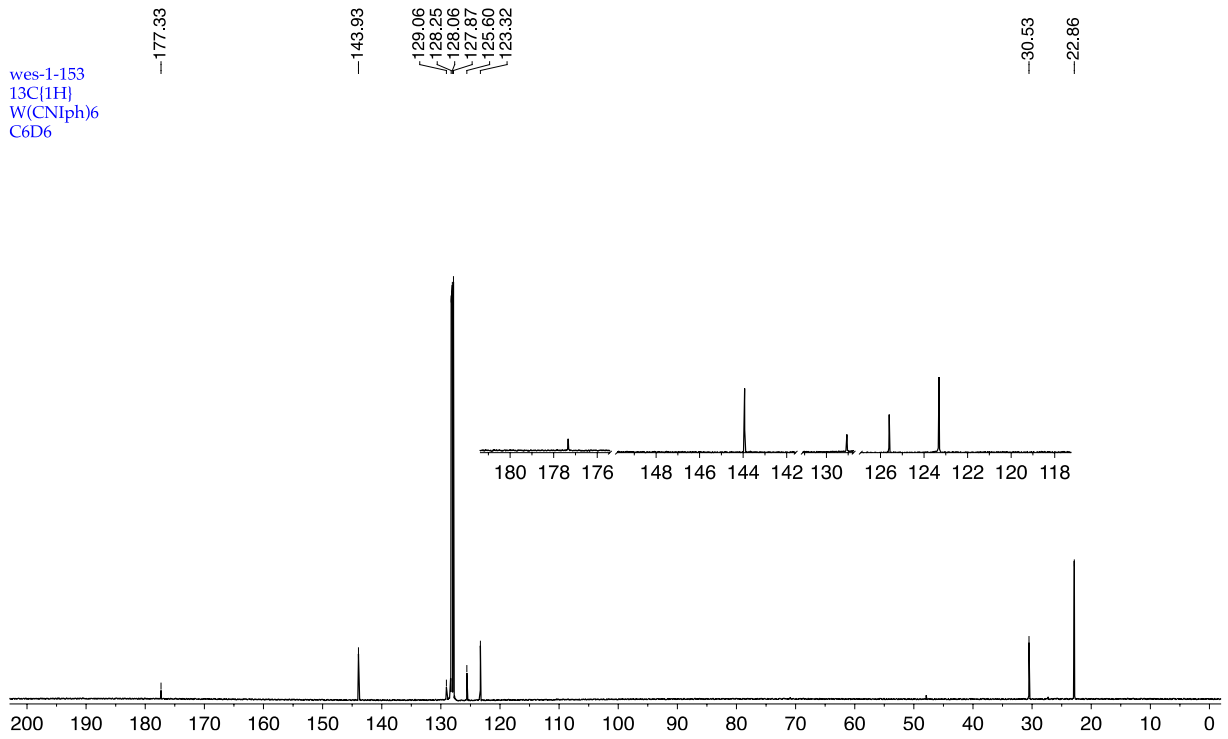


Figure S27. *$^{13}C\{^{1}H\}$ NMR of $W(CNIph)_6$*

References:

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(b) Warratz, R.; Peters, G.; Studt, F.; Römer, R.-H.; Tuczek, F. *Inorg. Chem.* **2006**, *45*, 2531-2542.